

# (12) UK Patent Application (19) GB (11) 2 141 932 A

(43) Application published 9 Jan 1985

(21) Application No **8415830**

(22) Date of filing **21 Jun 1984**

(30) Priority data

(31) **69070** (32) **24 Jun 1983** (33) **IL**

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(51) INT CL<sup>3</sup>  
**A61K 25/00**

(52) Domestic classification  
**A5E 300 322 326 CG  
U1S 1262 1275 1290 A5E**

(56) Documents cited  

<b>GB A 2129302</b>	<b>GB 1490137</b>
<b>GB A 2063068</b>	<b>EP A 0060589</b>
<b>GB 1548920</b>	<b>EP A 0005475</b>

(58) Field of search  
**A5E**

## (54) **Pest control**

(57) Compositions, for pest control by the disruption of the mating process of such pests, comprise a pheromone or a pheromone inhibitor in liquid or semi-liquid form, in a polymeric water-resistant matrix which provides UV protection, and which allows an adequate rate of diffusion of the active material over a prolonged period of time said composition being adapted to be applied to a solid support, which can be a part of a plant, such as leaves. A method of pest control in the field is based on the application of a plurality of spots of adequate size over a field, each such spot containing 2 to 10 mg of the active substance.

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## SPECIFICATION

## Pest Control Compositions

The invention relates to novel pest control compositions and to a novel method of pest control. Various pest control agents can be applied, the preferred ones being pheromones and pheromone inhibitors, specific for the pest to be controlled.

## Background of the Invention

The ecological problems related to the increased use of pesticides are well known. Contamination of soil and water is widespread. Toxic residues remaining for shorter or longer periods contaminate the crops, fruits and livestock, and through these routes endanger the health of humans.

As more becomes known about the toxicity of various pesticides, regulation of their use has become more stringent and some products have been completely banned. Since the use of pest-control materials is essential in order to protect the crops, many ways have been tried to improve the efficiency of their use, thus minimizing the amounts applied and consequently also decreasing the ecological impact. The methods used consist mainly in improved application techniques such as better formulations—using various surfactants, wetting agents, stickers (adhesives) etc.—or combinations in various forms and shapes with polymeric and other materials, to increase the effective duration of activity of pesticide in the field. For example pesticides have been applied in microcapsules, films, tapes, hollow fibers etc. In all cases the principle being that a matrix containing the active ingredient is distributed densely and as uniformly as possible over the crop to be protected.

Other methods for reducing the amounts of pesticides used consist of replacing them—at least partially—by biological control methods. One of these being the use of sex attractants, Pheromones, and also Pheromone-inhibitors. The theory behind the use of these materials is that by disrupting the normal mating process the pest population can be substantially reduced.

Pheromones have been used till now mainly in traps, for monitoring and in a very limited way for population control, the reason being that these substances which are extremely effective at very low concentrations, but also quite unstable under normal weather conditions, and are quickly degraded on exposure.

## State of Prior Art

There exist no effective ways for the large scale application of pheromones in the field. This is probably due to the fact that in all the methods mentioned above—microcapsules, tapes, etc.—a few gram per acre of the material are used. The wide coverage results in an intensive exposure to the environment of the Pheromone which is then quickly lost by evaporation, U.V. degradation and hydrolysis.

There exists a number of patents on the slow release of pheromones, most of them relate to microencapsulation or to mixtures with various materials to retard release and obtain combined effects, for instance by including insecticides in the formulation. U.S. Patent No. 3952093 (Roelof et al) discloses that pheromone formulations may be encapsulated and used in sprayable form.

U.S. Patent No. 3954968 (McKibben) teaches the use of a synthetic pheromone mixed with polyethyleneglycol or their derivatives. The formulation may be in the form of tablets or capsules.

U.S. Patents No. 3845108 and US 3852419 (Roelof et al) disclose the dispersion of pheromones in various diluents, including inert viscous liquids, to reduce their rate of volatilization.

U.S. Patent No. 3966902 (Chromacek) refers to different slow release polymer compositions. This patent relates only to insecticides encapsulated in the polymer and formulated as sprays. Albrect et al in U.S. Patent No. 4107318 discloses stable fungicidal dispersions which include mineral oils and dispersing agents.

A system for the controlled delivery of pheromones has been described (Kydonieous et al, Controlled Release Polymeric Formulations P. 285, American Chemical Society Symposium, Series 33, 1976). It is called the Hercon Tape and consists of a three-layer plastic laminate with the pheromone reservoir in the inner layer. The use of hollow fibers for dispensing pheromones has also been described in the same publication (Ashare et al p. 273).

None of the above methods are satisfactory from a practical point of view. Sprayed formulations of pheromones have a very short effective lifespan in the field. Tapes and hollow fibers are cumbersome to apply.

Microencapsulation is a relatively expensive process, requiring special techniques for its production.

## Summary of the Invention

In order to be useful for the protection to large crop areas, a pheromone for formulation would have to fulfill several conditions:

a) Application should be possible by equipment normally used in agriculture such as airplanes, tractors, etc.

b) The formulation, once applied, should have a lasting effect in the field (not less than say two weeks).

The effect of the Pheromones, as that of a number of pesticides, is due to evaporation of the active material and its arriving via the air streams to contact with the target insects.

## 5 Brief Description of the Invention 5

The invention relates to novel pest control agents and to a novel method of pest control. The preferred active ingredients used are pheromones and pheromone inhibitors, although other pest control agents may also be used.

The novel compositions are based on the active material being contained in a polymeric matrix adapted to provide for the gradual and controlled release of the active material, and which is characterized in that it provides protection against degradation and deterioration in the field, such as protection against UV and/or oxidation. The formulations have advantageously adequate adhesive properties to stick to supports. 10

The novel compositions can be applied in the form of various systems, such as solutions, aerosol formulations and the like, the results being the formation of a plurality of "spots", each of which consists of the active material in the polymeric matrix, which may contain certain adjuvants such as UV protective agents, antioxidants, adhesives, etc. each such "spot" containing (after evaporation of the solvent, if present) a minimum quantity of the active material. 15

This minimum has been found to be generally not less than about 2 mg per spot, and preferably from 5 to 20 mg of the active material per spot. The spots are applied in predetermined distribution over large areas, and disrupt communication between insects and thus their mating, resulting in a substantial decrease of insect population. Tests have shown that application of pheromones or pheromone inhibitors in the field give satisfactory results when the total quantity per 1000 m<sup>2</sup> (1 dunam) is from about 2 to 20 g the preferred range being about 3 to 10 g/1000 m<sup>2</sup>. The active material is applied in a number of discrete spots, each of which contains advantageously about 5 to 20 mg of the active material, the concentration in the polymeric matrix being from about 2 to about 20 weight per cent of the active ingredient. The formulations are such that no substantial degradation takes place over prolonged periods of time, and that after about 2 weeks there remains about 25% of the active material in the matrix. 20 25

The rate of degradation can be substantially decreased by concentrating in one spot larger quantities of the pheromone. (Z)-9-Tetradecen-1-ol-formate (TOF), Heliothis pheromone inhibitor, was formulated with a copolymer and applied in the form of discrete spots on filter paper squares (10×10 cm) at rates of respectively 2 and 5 mg per spot. These were exposed to the sun, wind and dew, and the remaining TOF was determined. Results were as follows: 30

35	% Of initial quantity remaining after:		35
	one day	four days	
	2 mg/spot	43	8.5
	5 mg/spot	87	62

Various copolymers can be designed which can protect the pheromones, or the pheromone inhibitors for long periods of time against the effects of the weather, allowing these active materials to slowly escape by diffusion through the polymeric matrix and thus be effective in the field over a long period of time, producing a continuous disruption of the mating process and consequently a reduction of the insect population. Since the population-control effect is due to evaporation of the active ingredient there is in fact no need to spread the formulation finely divided over a vast area. In fact, we have found that a much better effect is obtained when the formulation and mode of application are such that the active spots are concentrated at relatively large distances from each other. 40 45

The insect attractants (Pheromones) and pheromone inhibitors (disruptants) which can be used in the formulation of this invention, are of various chemical types. In general they consist of long chain hydrocarbons having one or more double bonds in various steric configurations. The chain ends either in an hydroxyl group or ester group. Other types of these compounds have a terminal aldehyde group. Some of these pheromones and inhibitors are listed below. 50

(E)-7-Dodecen-1-ol  
(Z)-8-Dodecen-1-ol  
(E)-8-Dodecen-1-ol  
55 (Z)-9-Dodecen-1-ol 55  
(E)-9-Dodecen-1-ol  
11-Dodecen-1-ol  
(Z,E)-5,7-Dodecadien-1-ol  
(E,E)-5,7-Dodecadien-1-ol

	(E,E)-8,10-Dodecadien-1-ol	
	(Z,E)-3,7,11-Trimethyl-2,6,10-dodecatrien-1-ol(Z,E)-farnesol	
	(E,E)-3,7,11-Trimethyl-2,6,10-dodecatrien-1-ol(E,E)-farnesol	
	3,7,11-Trimethyl-1,6-10-dodecatrien-3-ol(nerolidol)	
5	(Z)-7-Tetradecen-1-ol	5
	(Z)-8-Tetradecen-1-ol	
	(Z)-9-Tetradecen-1-ol	
	(E)-9-Tetradecen-1-ol	
	(Z)-10-Tetradecen-1-ol	
10	(Z)-11-Tetradecen-1-ol	10
	(Z,E)-9,12-Tetradecadien-1-ol	
	(Z)-7-Hexadecen-1-ol	
	(Z)-11-Hexadecen-1-ol	
	(E)-11-Hexadecen-1-ol	
15	(E,Z)-10,12-Hexadecadien-1-ol(bombykol)	15
	(E,E)-10,12-Hexadecadien-1-ol	
	(Z)-14-Methyl-8-hexadecen-1-ol	
	(E)-14-Methyl-8-hexadecen-1-ol	
	(Z)-13-Octadecen-1-ol	
20	(Z,Z)-3,13-Octadecadien-1-ol	20
	(E,Z)-3,13-Octadecadien-1-ol	
	3-Methyl-2-cyclohexen-1-ol(seudenol)	
	cis-2-Isopropenyl-1-methylcyclobutaneethanol(grandlure I)	
	(Z)-5-Dodecen-1-ol formate	
25	(Z)-7-Dodecen-1-ol formate	25
	(E)-7-Dodecen-1-ol formate	
	(Z)-9-Tetradecen-1-ol formate	
	(Z,E)-9,12-Tetradecadien-1-ol formate	
	(Z)-11-Hexadecen-1-ol formate	
30	2,6-Dimethyl-1,5-Heptadien-3-ol acetate	30
	(Z)-4-Decen-1-ol acetate(Z)-5-decen-1-ol acetate	
	(E)-5-Decen-1-ol acetate	
	(Z)-7-Decen-1-ol acetate	
	3-Methyl-6-(1-methylethenyl)-9-decen-1-ol acetate	
35	(Z)-3-Methyl-6-(1-methylethenyl)-3,9-decadien-1-ol acetate	35
	(E)-3,9-Dimethyl-6-(1-methylethenyl)-5,8-decadien-1-ol acetate	
	(Z)-7-Undecen-1-ol acetate	
	(Z)-8-Undecen-1-ol acetate	
	(Z)-5-Dodecen-1-ol acetate	
40	(Z)-5-Dodecen-1-ol acetate	40
	(Z)-7-Dodecen-1-ol acetate(E)-7-dodecen-1-ol acetate	
	(Z)-8-Dodecen-1-ol acetate	
	(E)-8-Dodecen-1-ol acetate	
	(Z)-9-Dodecen-1-ol acetate	
45	(Z)-9,11-Dodecadien-1-ol acetate	45
	(E)-9,11-Dodecadien-1-ol acetate	
	(Z)-7-Tridecen-1-ol acetate	
	(Z)-8-Tridecen-1-ol acetate	
	(E)-8-Tridecen-1-ol acetate	
50	(Z)-10-Tridecen-1-ol acetate	50
	(Z)-11-Tridecen-1-ol acetate	
	(E)-11-Tridecen-1-ol acetate	
	(E,Z)-4,7-Tridecadien-1-ol acetate	
	(E,Z,Z)-4,7,10-Tridecadien-1-ol acetate	
55	(Z)-11-Methyl-9,12-tridecadien-1-ol acetate	55
	(Z)-5-Tetradecen-1-ol acetate	
	(E)-6-Tetradecen-1-ol acetate	
	(Z)-7-Tetradecen-1-ol acetate	
	(E)-7-Tetradecen-1-ol acetate	
60	(Z)-8-Tetradecen-1-ol acetate	60
	(Z)-9-Tetradecen-1-ol acetate	
	(E)-9-Tetradecen-1-ol acetate	
	(Z)-10-Tetradecen-1-ol acetate	
	(E)-10-Tetradecen-1-ol acetate	
65	(Z)-11-Tetradecen-1-ol acetate	65

	(Z)-12-Tetradecen-1-ol acetate	
	(E)-12-Tetradecen-1-ol acetate	
	(Z,Z)-3,5-Tetradecadien-1-ol acetate	
	(Z,E)-3,5-Tetradecadien-1-ol acetate	
5	(E,E)-3,5-Tetradecadien-1-ol acetate	5
	(Z,E)-9,11-Tetradecadien-1-ol acetate	
	(E,E)-9,11-Tetradecadien-1-ol acetate	
	(E,E)-9,11-Tetradecadien-1-ol acetate	
	(Z,E)-9,12-Tetradecadien-1-ol acetate	
10	(Z)-12-Pentadecen-1-ol acetate	10
	(E)-12-Pentadecen-1-ol acetate	
	(Z)-7-Hexadecen-1-ol acetate	
	(Z)-9-Hexadecen-1-ol acetate	
	(Z)-10-Hexadecen-1-ol acetate	
15	(Z)-11-Hexadecen-1-ol acetate(E)-11-hexadecen-1-ol acetate	15
	(E,Z)-6,11-Hexadecadien-1-ol acetate	
	(Z,Z)-7,11-Hexadecadien-1-ol acetate	
	(Z,E)-7,11-Hexadecadien-1-ol acetate	
	(E,Z)-7,11-Hexadecadien-1-ol acetate	
20	(E,E)-7,11-Hexadecadien-1-ol acetate	20
	(Z,E)-11,14-Hexadecadien-1-ol acetate	
	(Z)-13-Octadecen-1-ol acetate	
	(Zm)-3,13-Octadecadien-1-ol acetate	
	(Z,E)-3,13-Octadecadien-1-ol acetate	
25	(E,Z)-3,13-Octadecadien-1-ol acetate	25
	(E,E)-3,13-Octadien-1-ol acetate	
	3-Methylene-7-methyl-7-octen-1-ol propanoate	
	(Z)-3,7-Dimethyl-2,7-octadien-1-ol propanoate	
	(Z)-3,9-Dimethyl-6-(1-methylethenyl)-3,9-decadien-1-ol propanoate	
30	(E,E)-8,10-Dodecadien-1-ol propanoate	30
	(Z,E)-9,12-Tetradecadien-1-ol propanoate	
	(Z)-9-Hexadecen-1-ol propanoate	
	2,4-Hexadienyl butanoate	
	(Z)-5-Decenyl 3-methylbutanoate	
35	1-Methylethyl (Z)-9-dodecenoate	35
	1-Methylethyl (Z)-9-tetradecenoate	
	Methyl (Z,Z)-3,5-tetradecadienoate	
	Methyl(Z)-hexadecenoate	
	1-Methylethyl (Z)-9-hexadecenoate	
40	Methyl (Z)-14-methyl-8-hexadecenoate	40
	Methyl (E)-14-methyl-8-hexadecenoate	
	1-Methylethyl (Z)-9-octadecenoate	
	(Z)-9-Hexadecenyl (Z)-9-octadecenoate	
	(E)-3,7-Dimethyl-1,6-octadienal geranial	
45	(Z)-3,7-Dimethyl-1,6-octadienal(neral)	45
	(Z)-7-Dodecenal	
	(Z)-9-Dodecenal	
	Tetradecanal	
	(Z)-5-Tetradecanal	
50	(Z)-7-Tetradecanal	50
	(Z)-9-Tetradecanal	
	(Z)-11-Tetradecanal	
	(Z)-11-Tetradecanal	
	(E)-11-Tetradecanal	
55	(E)-11-Hexadecanal	55
	(Z)-12-Hexadecanal	
	(Z)-13-Hexadecanal	
	(E,Z)-6,13-Hexadecadienal	
	(E,Z)-10,12-Hexadecadienal(bombykal)	
60	(E,E)-10,12-Hexadecadienal	60
	(Z,Z)-11,13-Hexadecadienal	
	(Z)-14-Methyl-8-hexadecenal	
	S-(Z)-14-Methyl-8-hexadecenal	
	(E)-14-Methyl-8-hexadecenal	
65	S-(E)-14-Methyl-8-hexadecenal	65

- R-(E)-14-Methyl-8-hexadecenal  
 (Z)-11-Octadecenal  
 (Z)-13-Octadecenal  
 (E)-13-Octadecenal  
 5 (Z)3,3-Dimethyl- $\Delta^{1-\alpha}$ -cyclohexaneacetaldehyde(Grandlure III) 5  
 (E)-3,3-Dimethyl- $\Delta^{1-\alpha}$ -cyclohexaneacetaldehyde(Grandlure IV)

The following is a list of some of the insects which can be controlled by the materials of this invention:

	Alfalfa looper	Introduced pine sawfly	
10	American cockroach	Mediterranean fruit fly	10
	Banded cucumber beetle	Nun moth	
	Boll weevil	Oriental fruit moth	
	Bollworm	Pink bollworm	
	Bronze orange bug	Queen butterfly	
15	Cabbage looper	Red-pine scale	15
	California red scale	Screw-worm	
	Codling moth	Silkworm	
	Cotton leafworm	Sod webworms	
	Cynthia moth	Stable fly	
20	Face fly	Sugar-beet wireworm	20
	Giant water bug	Tobacco budworm	
	Grayling butterfly	Tobacco hornworm	
	Greater wax moth	Yellow mealworm	
	Gypsy moth	Yellow-striped armyworm	
25	Honey bee	Virginia-pine sawfly	25
	House fly		

The polymers which can be used for this type of application advantageously fulfill the following conditions:

- 30 a) Provide good protection against U.V. degradation and hydrolysis;  
 b) allow for diffusion at the desired rate;  
 c) are non-toxic to warm-blooded animals;  
 d) are not phytotoxic;  
 e) are water-resistant.

35 The monomers which can be used for making such polymers are commercially available. There may be used esters of acrylic acid, of methacrylic acid, vinyl acetate, vinyl pyrrolidone, styrene, etc.

35 The method of application consists in applying the active formulation in the form of discrete spots having a relatively high content of pheromone or pheromone inhibitor. The diluent can serve as part of the propellants used for the dispersion of the material.

40 The preferred method used is to prepare the copolymers in solution, using a suitable volatile organic solvent, the preferred monomers being vinyl pyrrolidone, methyl methacrylate and a higher alkyl methacrylate such as lauryl methacrylate. Each of these monomers fulfills a specific function. The vinyl pyrrolidone constitutes the hydrophilic part of the polymer, improves adhesion and acts as a plasticizer (by water absorption) to facilitate film-forming on the leaves. Methyl methacrylate has good resistance to U.V. and weathering. Lauryl methacrylate is a highly hydrophobic material and it also improves the film-forming properties of the composition.

The properties of the copolymer can be adapted to the particular conditions of use by changing the proportions of the comonomers as is well known the art.

The preferred method of application is by preparing a concentrated solution containing polymer, the pheromone or pheromone inhibitor and additives, and spraying this solution in the form of large globules or spots by means of suitable means. Compressed gases, low-boiling liquids and other propellants can be used.

The preferred monomers and proportions thereof are: methyl methacrylate, 30—60%, lauryl methacrylate, 15—30%, vinyl pyrrolidone, 15—30%. The most preferred range being: methyl methacrylate 50—60%, lauryl methacrylate, 15—20%, and vinyl pyrrolidone 20—25%.

The monomers can be used in various combinations and proportions in order to obtain the required solubilization, diffusion and adhesion characteristics. Polymerization can be effected using the methods well known in the art such as bulk, emulsion, suspension, or solution polymerization.

As polymerization catalysts, peroxides, diazo compounds and similar materials well known in the art can be used. Various additives, such as antioxidants, U.V. absorbers, adhesives, etc., can also be incorporated in the formulations.

The solvent used should have a low boiling point and be non-reactive with the active material and may be chosen amongst others from the following types:

Hydrocarbons: such as lower alkanes, petroleum ethers, etc.; benzene, chlorinated hydrocarbons, dichloromethane, dichloroethane, chloroform, etc.; ketones, such as acetone; methyl ethyl ketone; alcohols.

The preferred solvents are low boiling chlorinated alkanes.

As propellants there can be used halogenated hydrocarbons, low boiling hydrocarbons (propane, butane), carbon dioxide, nitrogen or compressed air.

The following examples are not to be construed in a limiting sense, but are merely illustrative of the present invention. All parts are by weight-percent.

#### EXAMPLE 1

A copolymer of Methyl Methacrylate (50) Lauryl Methacrylate (20) was prepared by suspension polymerization in water (120) using polyvinylalcohol (0.3) as the suspension agent and a redox catalyst composed of sodium metabisulfite and potassium persulfate.

The resulting precipitate was dried. It had a glass transition temperature (tg calculated) of 39°C. 25 g of the above polymer were dissolved in 225 g acetone, to this was added 1 g of the Heliotis pheromone inhibitor tetradecenol formate (TOF) and 25 g Aerosil 200 (fumed silica).

Samples of the above formulation were applied to filter-paper strips in 3 to 5 mg active material spots and showed good stability to evaporation: after 26 days at room temperature, 48.7% of the original inhibitor was still present.

#### EXAMPLE 2

A solution polymer was prepared composed of vinyl pyrrolidone (25) lauryl methacrylate (15) methyl methacrylate (60). The solvent used was isopropanol and the catalyst bis-azoisobutyronitrile.

The resulting solution was dried. 10 g of the above polymer were dissolved in 20 g dichloroethane. Added 538 mg tetradecenol formate, 215 mg butylated hydroxyanisole and 21 g cyanosorb (U.V. absorber).

A sample of the above formulation when exposed to the weather for 96 hours retained 71% of its initial active content.

#### EXAMPLE 3

A copolymer as per Example 2 was used.

240 g of the polymer were dissolved in 480 g dichloromethane and added to this solution 50 g tetradecenol formate.

100 g of the above mixture were put in an aerosol can, closed with a spray valve and pressurized with carbon dioxide to a pressure of 6 atmospheres.

Spots of this formulation were applied by spraying on filter paper strips. When these were exposed to the weather for 60 hours they still retained 43% of the original active ingredient content. When applied to a cotton field this formulation disrupted insect communication for more than 17 days as described below.

A field trial was made on a field of cotton infested with Heliotis and irrigated by aspersion on a 10 days cycle.

The formulation was applied to the plants at the rate of 5 g of active ingredient per 1000 m<sup>2</sup>. Around the treated field were located traps loaded with synthetic Heliotis pheromone. Disruption was indicated by the relationship between the number of insects trapped in the treated area and the number of insects trapped in the non-treated area. On the 16th day after treatment there was still a 96% disruption in the treated area.

In another trial on a cotton field (2 acres) infested by Heliotis zea and Heliotis Virescens, 800 g of the above formulation were applied at the rate of about 160 point sources per acre. Trapping and

mating reduction were observed. Thus, in *Heliothis zea*, 16 days after application there was still a 97% reduction in trapped insects (as compared to the untreated field) and a 100% reduction in mating. In *Heliothis Virescens* the comparative figures were 70% and 100% respectively.

#### EXAMPLE 4

5 The pheromone inhibitor cis-9-tetradecenyl acetate (cis-9-TDA) was used as the active ingredient. A number of polymers were used in conjunction with this material. Tests showed results as follows:

	Polymer	Outdoors Exposure Time (hours)	% Remaining of Original Content	
10	Polystyrene	144	26	10
	Poly(lauryl methacrylate)	17	40	
	Poly(styrene-lauryl methacrylate, 85/15)	42	0	
15	Poly(styrene-lauryl methacrylate 85/15) with antioxidant 2,5-diterbutyl hydroquinone	48	11	15

#### EXAMPLE 5

A solution polymer was made composed of vinyl pyrrolidone (25), lauryl methacrylate (15) and methyl methacrylate (60). The solvent used was dichloromethane.

20 The solution was diluted to a solids content of 33%. To 3.6 g of this solution were added 0.25 gr of (Z,Z)-7,11-hexadien-1-ol acetate. 20

200 mg of this solution were applied to filter paper strips and these were put on a roof fully exposed to the weather. As a control a similar formulation was prepared but without polymer. Results obtained were as follows (in % of remaining active substance)

	Day	Without Polymer	
25	0	100	25
	1	49.6	
	3	0	
	5	0	
30	8	0	30
	With Polymer		
	0	100	
	2	67	
	5	47	
35	8	35.8	35

#### EXAMPLE 6

(Z,E)-9,11-Tetradecanienyl acetate was formulated with the polymer solution, as defined in Example 5 and subjected to the same test. Results were as follows:



	Day	Without Polymer	With Polymer	
	0	100	100	
	2	2.2	75	
	5	—	50	
5	8	—	12.5	5

#### EXAMPLE 7

Two preparations were made, similar to that of Example 5 but using as active ingredient Z-11-hexadecenal, one of these contained also 0.04% Cyanosorb-UV5411 (American Cyanide). Results after exposure to weather were as follows:

	Day	Without Polymer	With Polymer	With Polymer+ Cyanosorb	
10	0	100	100	100	10
	1	9.5	—	—	
	3	0	21.2	72	
	5	—	5.7	44.8	

15 Various other pheromones and pheromone inhibitors gave good results. The "spots" of active material in the polymer matrix (with required adjuvants or additives) were applied at a rate of about 3 to 20 g/100 m<sup>2</sup> in the open field (by distributing paper or other carrier sheets with "Spots" or by applying such "spots" to natural carriers in the field. Disruption of insect communication was achieved over periods exceeding 2 weeks when spots of about 5 mg active material per spot were used. 15

20 In one experiment about 30 spots were used per 1000 m<sup>2</sup> and good results were obtained. The active material comprises generally about 2 to 20 weight per cent of the matrix. 20

The novel composition can also be applied in the form of globules or the like consisting of the active material in the matrix, and these can be easily distributed over large areas.

25 Many variations and modifications can be resorted to without departing from the scope of the invention. 25

The polymers which can be used for this type of application advantageously fulfill the following conditions:

- a) provide good protection against U.V. degradation and hydrolysis;
- b) allow for diffusion at the desired rate;
- 30 c) are non-toxic to warm-blooded animals; 30
- d) are not phytotoxic;
- e) are water-resistant.

35 The monomers which can be used for making such polymers are commercially available. There may be used esters of acrylic acid, of methacrylic acid, vinyl acetate, vinyl pyrrolidone, styrene, etc. The monomers can be used in various combinations and proportions in order to obtain the required solubilization, diffusion and adhesion characteristics. Polymerization can be effected using the methods well known in the art such as bulk, emulsion, suspension, or solution polymerization. 35

40 As polymerization catalysts, peroxides, diazo compounds and similar materials well known the art can be used. Various additions, such as antioxidants, U.V. absorbers, adhesives, etc., can also be incorporated in the formulations. 40

#### CLAIMS

1. A composition for pest control by disruption of the mating process of the insects to be controlled, which comprises a pheromone or pheromone inhibitor in a liquid or semi-liquid polymeric water-resistant matrix providing UV protection, allowing an adequate rate of diffusion of the active material over a prolonged period of time, said composition being adapted to be applied to a suitable support. 45

2. A composition according to claim 1 wherein the pheromone or pheromone inhibitor is of the unsaturated hydrocarbon type bearing a terminal hydroxy, ester or aldehyde group, comprising from 2 to 20 weight-% of the composition.

50 3. A composition according to claim 1 or 2, wherein the polymer or copolymer affords UV protection or where the composition contains a UV-protection and optionally an antioxidant, an adhesive agent. 50

4. A composition according to any of claims 1 to 3, wherein the polymeric matrix is a copolymer of a hydrophobic and a hydrophilic monomer.
5. A composition according to any of claims 1 to 3, wherein the polymeric matrix is a polymer or copolymer resulting from the polymerization of monomers selected from vinyl pyrrolidone, esters of acrylic or methacrylic acid, vinyl acetate and styrene. 5
6. A composition according to any of claims 1 to 5, in the form of a sprayable composition adapted to provide spots of a content of active material of from 2 to 10 mg.
7. A composition according to claim 6, in the form of an aerosol spray containing a solvent and/or propellant.
- 10 8. A composition according to claims 1 to 9, wherein the active ingredient is selected from (Z)-9-tetraden-1-ol-formate, (Z,Z)-7,11-hexadien-1-ol-acetate, (Z,E)-9,11-tetradecadienyl acetate, Z-9-tetradecenyl acetate and Z-11-hexadecenal. 10
9. Compositions for applying pheromones or pheromone inhibitors, adapted to provide for the formation of spots containing at least 2 mg of the active material per spot in a suitable polymeric matrix, substantially as hereinbefore described and with reference to any of the Examples. 15
10. A method of pest control which comprises applying in the field a predetermined number of localized "spots" comprising a suitable pheromone or pheromone inhibitor in a polymeric matrix providing UV protection and adequate adhesion to the substrate, yet permitting an adequate rate of diffusion of the active ingredient into the atmosphere, each such spot containing at least 2 mg and preferably 5 or more mg of the active ingredient. 20
11. A method according to claim 10, wherein a liquid or semi-liquid composition is used as defined in any of claims 1 to 9.
12. A method according to any of claims 10 or 11, wherein the number of "spots" is about 10 to 100 per 1000 square meters.
- 25 13. A method according to any of claims 10 to 12, wherein the quantity of active pest control agents is from 1 to 10 grams per 1000 square meters. 25
14. Method of pest control according to any of claims 10 to 13, wherein the spots of active material in the polymeric matrix are applied by spraying to plants, and preferably to leaves.
15. Method of pest control by means of pheromones and pheromone inhibitors in a polymeric matrix substantially as hereinbefore described and with reference to the Examples. 30